Triple point of gallium as a temperature fixed point

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The triple-point temperature of high-purity gallium has been determined to be 29.77398 °C using five standard platinum resistance thermometers (SPRTs), recently dried and then calibrated on the IPTS-68, and using ten samples of gallium from three commercial sources. All data obtained on the highest-purity sample have a standard deviation of ±0.00014 °C and the systematic uncertainty is estimated to be ±0.0006 °C. Three of the samples investigated were in all-plastic cells and seven samples were in steel cells with Teflon containers for the gallium and with Teflon-coated stainless-steel thermometer wells. Intercomparisons of the triple-point temperatures of all ten samples, each of a different lot, were made for several different gallium mantles of each sample.

INTRODUCTION

We report here the results of the continuation of our investigation[1] of the suitability of the triple point of pure gallium as a defining temperature fixed point of the International Practical Temperature Scale[2]. Although the abundance of gallium in the earth's crust is only about 5 to 15 parts per million and is widely dispersed, gallium is readily available commercially at very high purity and at a relatively low price. Consequently, samples of gallium suitable for use in fixed-point cells are readily available to anyone.

Gallium was first isolated[3] in 1875 and several melting-point temperature determinations were subsequently made[4-8]. Since gallium became commercially available at high purity, it has been used in numerous studies of melting behavior[9-14] and there have been several determinations of its melting-point or freezing-point temperature[13,15-18] and of its triple-point temperature[1]. Its pressure dependence has also been measured[1,17].

The investigation reported here was undertaken (1) to determine the possible variation of the triple-point temperature with different gallium mantles of the same sample for 10 samples from 3 sources, (2) to investigate the variation of triple-point temperature from lot to lot, (3) to determine the triple-point temperature of the highest-purity sample to the highest possible accuracy using five standard platinum resistance thermometers (SPRTs)[19] recently dried and calibrated, and (4) to investigate the use of steel cells relative to all-plastic cells.

EXPERIMENTAL
Gallium Samples

The ten gallium samples studied in this investigation were obtained from three sources - Alcoa, Alusuisse and Eagle-Picher.* Three of the samples were the same as those on which we reported earlier[1]. Of the ten samples studied, seven were from Alcoa, two were from Alusuisse and one was from Eagle-Picher. The six new samples from Alcoa and the one new sample from Alusuisse were stated by the manufacturers to be 99.9999+% pure and 99.99999% pure, respectively. The sources, lot numbers and nominal purity of the samples are listed in Table I. One sample from each of the three sources of gallium, lot numbers 3809B, F17/220 and J-57-76, constituted the three samples of gallium on which we reported earlier[1]. The purities as specified by the suppliers are difficult, if not impossible, to verify.

Table I. Specifications of Gallium Samples

Source	Lot Number	Nominal Purity
Alcoa	3809B	99.9999+% (Semiconductor grade)
	3854	99.9999+% (Semiconductor grade)
	3855	99.9999+% (Semiconductor grade)
	3856	99.9999+% (Semiconductor grade)
	3860	99.9999+% (Semiconductor grade)
	8002	99.9999+% (Semiconductor grade)
	8005	99.9999+% (Semiconductor grade)
Alusuisse	F17/220	99.9999+% (Microwave grade)
	F17/252	99.99999+%
Eagle-Picher	J-57-76	99.99999%

Gallium and Water Triple-Point Cells
Gallium Triple-Point Cells

Although the all-plastic cells described previously[1] have the very desirable feature that the possibility of metallic contamination of the gallium from components of the cells is eliminated, they have the undesirable features that plastics are permeable to gases and moisture and are much less rugged than steel cells. The latter features are not serious problems in most standards laboratories, where facilities for pumping the all-plastic cells (during their use) and for filling the cells with dry argon (after their use) are usually available. Since such facilities might not be available for many possible users, however, we decided to test the feasibility of using steel cells, which could be evacuated and sealed. These would be easier to use than the all-plastic cells and would require fewer facilities for their proper operation and the realization of the gallium triple-point temperature.

The all-plastic cells containing samples 3809B, F17/220 and J-57-76 have been described in detail previously[1] and will not be described again here. The cells for the other seven samples were very similar in design to the all-plastic cells. The material of construction, as stated above, however, was different except the Teflon container in which the gallium was held. The outer cases of the cells were Teflon-coated steel. The cap assembly, which consisted of the cap, the re-entrant thermometer-well tube, the pumping tube and a valve, was constructed of stainless steel and, with the exception of the valve, was Teflon-coated. The

cap was attached to the outer case of the cell by means of an O-ring seal and was held in place by 8 screws passing through the outer rim of the cap into the outer case. The inner container held the gallium and, as stated above, was made of Teflon. Its design was very similar to that used in the all-plastic cells, the difference being the addition of a splash cap. The latter was hollow with each side of the cap containing a small hole through which the space above the sample could be evacuated. The holes were located π radians apart.

The thermometer well (Teflon-coated stainless-steel tube, 3/8 inch in diameter with 0.005 inch thick walls) of each cell contained a welded-in-place and Teflon-coated stainless-steel bushing, 0.032 inch thick and 5 cm long, in the bottom of the well to provide contact between the SPRTs and the gallium.

Before the cells were assembled, the Teflon and Teflon-coated components were soaked overnight in aqua regia, thoroughly rinsed in distilled water and then air dried. The cap assembly was not attached to the base of a cell until the cell had been filled with the gallium sample.

The cells were filled with the gallium samples in a glove box containing a dry argon atmosphere. The liquefied gallium was poured into the Teflon containers of the cells directly from polyethylene squeeze bottles in which the gallium had been sealed under argon by the suppliers. Approximately 900 grams of gallium were put into each cell. After a gallium sample was poured into a cell, the cap assembly was attached to the base of the cell, the valve closed and the gallium solidified by decreasing the temperature of the glove box to 29 °C, or lower, and inserting a liquid-nitrogen-cooled copper rod into the thermowell several times. The solidification process was monitored by a thermometer which was periodically placed in the thermowell.

Water Triple-Point Cells

One triple point of water cell, B-11-803, obtained from Jarrett, Inc. (USA) was used in all of the determinations of the gallium triple-point temperature.

Equipment
Thermometers

Five SPRTs purchased from Leeds and Northrup were used in this investigation. Two of them (L&N 8167-25 Series) had platinum elements that consisted of a single layer helix of bifilarly-wound platinum wire on a mica cross. The other three SPRTs (L&N 8163 Series) had platinum elements consisting of a coiled helix of platinum wire mounted on a mica cross. Pertinent information regarding the five SPRTs is given in Table II, in which S/N refers to the serial number and NBS I.D.# refers to the NBS identification number.

Prior to this investigation, the heads of the SPRTs had been modified for ac measurements by the removal of the external copper leads, provided by the manufacturer for dc measurements, and the installation of BNC connectors mounted in bakelite caps. These were connected to the diagonal pairs of platinum wires which came up the stems of the SPRTs from the helical elements in a square array and passed through hermetic seals. By this arrangement, one coaxial cable served as the current leads and the other served as the potential leads. The SPRTs' resistances were insensitive to lead positions.

We had some evidence before this study began that some of the SPRTs probably contained moisture. Consequently, SPRTs 089, 090, 369, 374 and 375 were opened, connected to a high vacuum system and evacuated. Once a good vacuum was obtained, the SPRTs were heated to 225 °C and maintained at that temperature for about 2 to 3 days, but, in any case, until the pressure was down to $<10^{-5}$ Pa. When the pressure reached the range of 10^{-5} to 10^{-6} Pa, the furnace was de-energized and the SPRT in the furnace permitted to cool overnight. Then, a mixture of 90% Ar and 10% O_2 was admitted into the SPRT to a pressure of 50 kPa and the SPRT sealed. The SPRTs

Table II. Description of SPRTs Used in the Investigation

SPRT S/N	NBS I.D.#	SPRT Type	Date Calibrated	Calibration Constants	
				α	δ
1808364	089	8163	Jan. 1977	3.925683×10^{-3}	1.497137
1808366	090	8163	May 1977	3.926196×10^{-3}	1.496878
			Nov. 1979	3.926191×10^{-3}	1.496847
1808369	369	8163	May 1977	3.926181×10^{-3}	1.496823
			Nov. 1979	3.926166×10^{-3}	1.496850
1846677	374	8167-25	Jan. 1977	3.926390×10^{-3}	1.496519
			Nov. 1979	3.926354×10^{-3}	1.496427
1846729	375	8167-25	Jan. 1977	3.926079×10^{-3}	1.496538
			Nov. 1979	3.926073×10^{-3}	1.496586

were then calibrated, without any further annealing, by the NBS Platinum Resistance Thermometer Calibration Laboratory at measuring currents of 1 and 2 mA, with extrapolations to zero current. The zero-current calibrations were then used in all calculations of temperature, thereby eliminating self-heating effects in all of the measurements.

The thermometers had a slightly smaller amount of self-heating in the steel cells than they did in the all-plastic cells. For example, with a measuring current of 1 mA, SPRTs 374 and 375 had self-heatings of $\sim$0.85 m°C in the all-plastic cells and $\sim$0.75 m°C in the steel cells. Similarly, SPRT 369 had a self-heating of $\sim$2.15 m°C in the all-plastic cells and $\sim$2.00 m°C in the steel cells.

Constant Temperature Bath

The constant temperature bath and the control system used in this investigation is the same as that described previously[1]. Through the use of this system, temperatures were maintained uniform and constant to ±1 m°C, or better.

Resistance Bridges

An ac resistance-ratio bridge[20] and a dc resistance-ratio bridge[1] were used to measure the resistances of the SPRTs. The ac bridge, designed and built at NBS[1], operates at 400 Hz and is stated to be in error by no more than 3 $\mu\Omega$ when used with a 100 Ω standard resistor[20]. The resolution obtained with this bridge, operating at measuring currents of 1 and $\sqrt{2}$ mA and using a standard resistor of 100 Ω as the reference resistor, was ±0.15 $\mu\Omega$ when the output signal was displayed on a strip-chart recorder.

Since a dc Mueller bridge was used in calibrating the SPRTs, dc techniques were also used in making measurements in this investigation. A Guildline Current Comparator, Model 9975, was used for this purpose. This bridge has an automatic current reversal feature, with reversal periods of 4, 8 or 16 seconds. All measurements made with this bridge during this investigation were made with a 4 second reversal period. The dried thermometers had been previously checked in the triple-point of water cell at 4 and 16 second reversal periods and no differences were observed in the bridge readings. The inaccuracy of the current comparator was stated by the manufacturer to be <2 parts in 10^7 plus 1 digit in the last (8th) dial. Using a 3-second time constant and averaging the strip-chart recording of the bridge output

for 10 minutes gave a bridge resolution of ± 1.5 μΩ (± 15 μ°C) at measuring currents of 1 and $\sqrt{2}$ mA.

Only the ac bridge was used for the investigation of the immersion characteristics of the SPRTs in the different types of cells and for the study of the melting behavior of the samples. Both the ac and the dc bridges were used for direct comparisons of the different gallium samples and for the measurements of the triple-point temperature.

Standard Resistor

The standard resistor used as the reference resistor for both resistance bridges was a 100 Ω precision resistor, Model No. HA518, which we designated as H19, manufactured by Vishay. It was encased in an aluminum block which, in turn, was enclosed by and thermally shielded from a large copper container, the temperature of which was controlled at 27.75 ± 0.1 °C through the use of a mercury thermostat. Based on measurements of similarly enclosed resistors, a temperature variation of about ±3 m°C over a period of several days was estimated for H19. Using this estimate of temperature variation and using an estimated temperature coefficient of resistance of about 0.1 to 0.3 ppm/°C for the resistor at its regulated temperature, values which are based on the manufacturer's specifications, the variation of resistance of H19 was calculated to be $\leq \pm 0.1$ μΩ. Although the resistance value of the standard resistor is not used in the determination of temperatures, the resistor was calibrated at 400 Hz and at dc by the Absolute Electrical Measurements Section of the NBS on 9 February 1977 and on 21 March 1978. Over the period of time between calibrations, the 400 Hz and the dc resistances of H19 increased by 0.12 and by 0.10 ppm, respectively.

Vacuum System

The vacuum and gas handling system, by means of which the gallium cells were evacuated during the experiments and, for the nylon cells, filled with argon upon completion of an experiment, consisted of a mechanical rotary pump, a mercury manometer, an oil manometer, two alcohol-solid-carbon-dioxide mixture cold traps, manometer bypasses and some valves as described in detail previously[1]. Since dT/dP = -2.011 m°C/atm for gallium, it is not necessary to have a high vacuum in order to realize experimentally the triple-point temperature. With the simple system described above, the pressures obtained were sufficiently low that the uncertainty in the triple-point temperature from this source was <0.1 μ°C, well below our resolution. During the investigation reported here, the manometers were closed off from the remainder of the system and bypassed. A cold trap was located between the gallium cell or cells connected to the system and the other parts of the system. This ensured that the gallium was protected from contamination, even if the manometers were open to the system. All argon gas entering the gallium cells passed through the cold traps.

Measurements and Procedures
Preparation and Maintenance of Water Triple Points

Only one water triple-point cell was used in this investigation. It was obtained in February 1979. Triple points were prepared through the use of a liquid-nitrogen-cooled copper tube followed by the use of a heat pipe cooled by a solid carbon dioxide and ethyl alcohol mixture, as described in a previous publication[1]. Cracking of the mantle was avoided (1) by using only modest amounts of dry ice in the operation of the heat pipe (in order to give a slow, steady growth of the mantle), and (2) by terminating the freeze after the mantle reached about 1 cm in thickness, as viewed through the water. Several hours after terminating the freeze, the thermometer well of the cell was appropriately filled with chilled water, a small piece of foam rubber was placed in the bottom of the well to cushion the SPRTs from shock when they were being

inserted into the well, and a chilled aluminum bushing, 5 cm long, was inserted into the well to improve thermal contact between the inner liquid-solid interface and the SPRTs. The bushing fitted relatively snugly into the well and around the SPRTs. The cell so prepared was kept in a Styrofoam jacket which in turn was kept packed in ice in a dewar. During the measurement period, the cell was checked at least every morning to ensure that the ice mantle was free to rotate and not frozen to the thermometer well.

Preparation and Maintenance of Gallium Triple Points

In preparation for a comparison of the gallium triple-point temperatures of a given set of mantles of the samples, the following procedures were used. The all-plastic cells, with an atmosphere of argon above the gallium, were kept in ∿50 °C oil overnight in order to totally melt the gallium. The cells were then removed from the hot oil, placed in air, and allowed to cool to ∿29 °C. A mantle was then prepared by first initiating a freeze of the gallium by repeated insertions into the thermometer well of the cell a liquid-nitrogen-cooled copper tube, and then, after initiation of the freeze, putting the cell of solidifying gallium into a dewar containing a small amount of ice at the bottom. The cell was then covered at the top so that the mantle grew upward and outward from the bottom part of the thermometer well. The freezing process from initiation to completion required several hours. After the solidification was complete, the gallium triple point was prepared by placing the cell, containing the solid gallium under an atmosphere of argon, in an oil bath at ∿60 °C. The hot oil was more or less continuously pumped into the thermometer well, maintaining an average temperature of ∿40 °C, to ensure that there was an inner and an outer liquid-solid interface the full length of the column of gallium. After 20 minutes, during which time about 25 to 50% of the sample was melted, the cell was placed in a constant temperature oil bath at a temperature ∿10 m°C above the gallium triple-point temperature. Before measurements began, the cell was connected to the vacuum system and evacuated. Pumping of the cell continued throughout the measurements.

The gallium samples in the steel cells were similarly treated, except that they were always kept under a vacuum and except that in the preparation of the gallium triple point, the cells were kept in the 60 °C oil for only 6 minutes. They too were pumped during measurements.

After completion of comparison measurements on a set of mantles, the gallium samples were totally melted again and the process described above repeated, beginning with the preparation of a new set of mantles.

Following the comparison of the gallium samples, the triple-point temperature was determined from a set of measurements on the Alusuisse sample (F17/220) in the all-plastic cell. For these measurements, the triple-point was prepared as described above.

Thermal contact to the SPRTs was provided by the oil in the thermometer wells in the all-plastic cells and by the oil plus the bushings in the steel cells.

Temperature Measurements

The immersion study, the melting behavior and the comparison of the samples were made with only one SPRT, but the determination of the triple-point temperature involved the use of 5 SPRTs.

The triple-point temperature was determined from resistance ratio measurements of the 5 SPRTs in the Alusuisse sample (F17/220) at the triple point in the all-plastic cell, and in the water triple-point cell. Normally, 4 SPRTs were cycled through the gallium and water triple-point cells each day. The measurement sequence consisted of an SPRT being preheated in the oil bath containing the gallium cell for at least 30 minutes, then placed in the gallium cell. After the SPRT had been in the gallium cell for at least 30 minutes, its ac and dc resistance ratios were measured. Following these

measurements, the SPRT was removed from the cell, and then precooled in an ice bath for at least 30 minutes before being placed in the water triple-point cell. After being in the cell for at least 30 minutes, the ac and dc resistance ratios of the SPRT in the water triple-point cell were then measured.

Each time the resistance ratio of an SPRT was measured, its power dependence was determined by making measurements at 1 and $\sqrt{2}$ mA of measuring current. A 10 minute integration time was used for both ac and dc measurements and, in addition, a 3 second time constant was used for the dc measurements. The zero-power values of the SPRTs were used in the calculation of the triple-point temperature.

SPRT Immersion and Hydrostatic Head Effects

The immersion characteristics of the SPRTs in the all-plastic cells have been reported previously[1]. The behavior in the steel cells was very similar, as shown in Fig. 1. Measurements were made with SPRT 374 using the Cutkosky bridge[20]. Measuring currents of 1 and $\sqrt{2}$ mA were used, with extrapolation to zero current. The triple point for the immersion study was prepared as described earlier. Measurements were made on extraction and on insertion of the SPRT, using increments of 0.5 to 1 cm. When the SPRT was fully inserted into the thermometer well, the center of the platinum sensing element was approximately 13.5 cm below the top surface of the gallium. The temperature of the bath was ~10 m°C above the gallium triple-point temperature. As seen from Fig. 1, the effects of the temperature outside the cell were no longer discernible when the tip of the thermometer was within about 7.5 cm of the bottom of the well.
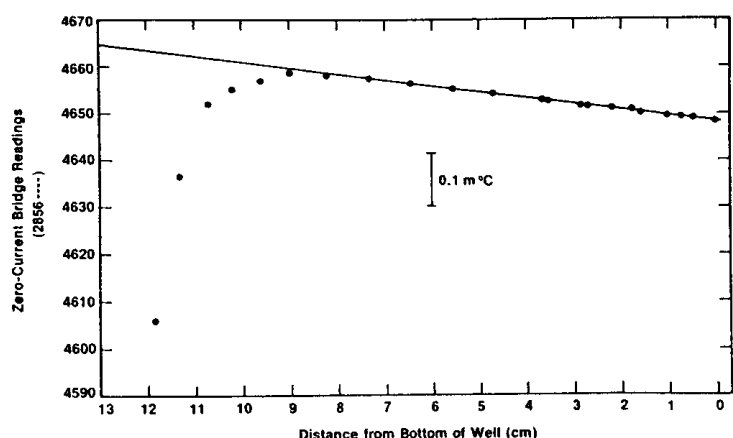

FIG. 1. Immersion characteristics of SPRT 374 in a steel triple-point cell containing gallium sample 3860 at the triple-point temperature. The data have not been corrected for hydrostatic head effects. The solid line, calculated from the measured pressure dependence of the melting point, has a slope corresponding to the effects of the hydrostatic pressure of the column of liquid gallium, i.e., -12 μ°C per cm of liquid gallium.

The hydrostatic head effect, i.e., the change of the melting temperature with the distance of the SPRT from the bottom of the well, is in excellent agreement with the results reported earlier[1], both the direct measurements of the effect and that calculated from the results of the melting temperature versus pressure experiments.

Gallium Melting Experiments

Melting behavior of the gallium in the all-plastic cells has been reported previously[1]. The melting behavior of the gallium in the steel cells was measured

in a fashion similar to that used for the all-plastic cells. An oil bath with a temperature held constant at ~40 °C was used for these measurements. The thermometer used in this phase of the study was SPRT 374, at a measuring current of 1 mA. From consideration of the design of the cells, it was clear that the principal point of thermal contact between the bath and the gallium would be at the bottom of the cell. Consequently, in order to reduce heat flow at that point and to prevent premature melting of the gallium at the bottom, a Styrofoam jacket was fitted to the bottom half of the cell. With such an arrangement, at least 3 melting curves were obtained for each cell, with at least 2 of the 3 melts being obtained for the samples after the mantles had been prepared in the standard way, as described earlier. This was to check for reproducibility of the melting behavior. Some melting curves were also obtained for samples after the triple points had been prepared. The purpose of the latter was to check for stability of the triple-point temperature and to check for its independence of the fraction of gallium melted.

Direct Comparisons of the Different Gallium Samples

Intercomparisons of the triple-point temperatures of the 10 gallium samples were made for 6 different mantles of each sample. This was accomplished by making a direct comparison of each sample with the Alusuisse sample (F17/220) in the all-plastic cell. These measurements did not involve measurements at the water triple point. After completion of the comparison of the triple-point temperatures of a given set of mantles, the gallium in each cell was totally melted and then frozen again in the way described earlier. The triple point of each new mantle was then prepared in the standard manner and a comparison of the triple-point temperatures of that set of mantles was conducted. The thermometer involved in these measurements was SPRT 375. Both ac and dc techniques were used, with measuring currents of 1 and $\sqrt{2}$ mA being employed to permit extrapolation to zero current for comparison purposes. Intercomparisons of the samples were made two at a time, with 5 dc and 2 ac sets of comparisons being made on each pair of mantles. A full day of measurements was required for a comparison of a pair of gallium mantles.

Measurement of the Gallium Triple-Point Temperature

As described earlier, 5 SPRTs were used in these measurements. Seven determinations were made with SPRT 089, 19 with each of SPRT 090 and SPRT 369, and 20 with each of SPRT 374 and SPRT 375. Two different gallium mantles of the Alusuisse sample (F17/220) in the all-plastic cell were involved in the measurements. The cell was pumped continuously and kept in a bath maintained ~10 m°C above the triple-point temperature. The measurements were conducted over a period of about two months.

RESULTS AND ANALYSIS
Immersion and Hydrostatic Head Results

The results of SPRT 374 immersion and the hydrostatic head measurements on gallium sample 3860 in one of the steel cells are shown in Fig. 1. These results are in agreement with those reported previously[1] for gallium in the all-plastic cells. When the tip of the thermometer (SPRT 374) was within about 7.5 cm of the bottom of the well, the thermometer was not influenced by the external environment of the cell. Below that depth of immersion, only the hydrostatic head effects were being observed and these results yield a value of -12 μ°C per cm of gallium, at the triple-point temperature, in agreement with the value of dT/dP = -2.011 m°C/atm reported previously[1].

Melting Behavior of the Gallium Samples

As indicated earlier, at least two melting curves were obtained for each sample of gallium in the steel

cells after the gallium had been frozen in the usual way. The general features of the curves, a typical one being shown in Fig. 2, were very similar to those obtained for the gallium samples in the all-plastic cells and which have been reported previously[1]. After the cells, with the SPRT, were placed in the 40 °C bath, the temperature, on a fairly coarse scale (uppermost curve of Fig. 2), very rapidly attained a nearly constant value at which it remained for about 8 hours (7 hours for the all-plastic cells). It then fairly slowly increased by about 0.5 °C over the next 1 1/2 to 2 hours before increasing very rapidly and approaching the bath temperature. On a scale having 250 times better resolution than that just described, the temperature (middle curve of Fig. 2) began increasing fairly slowly some 4 1/2 hours after melting began. The rate of change in temperature continuously increased until the increase became quite rapid some 7 hours after melting began. On a scale having yet 100 times greater resolution, the temperature (the bottommost curve) began increasing rather rapidly some 4 hours after melting began.
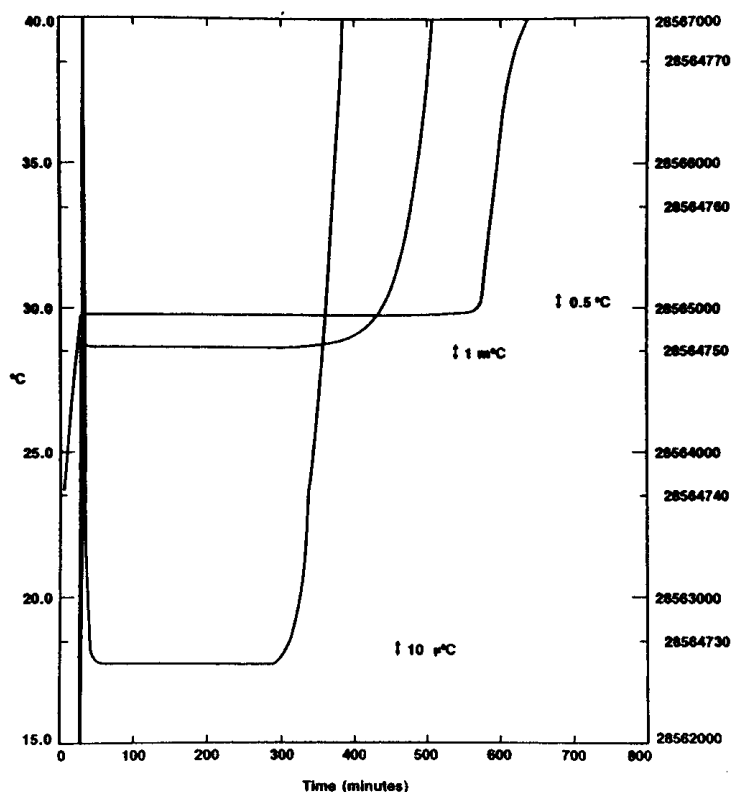

FIG. 2. Melting curve at three levels of resolution obtained with SPRT 374 for sample 3856 in a steel cell in a 40 °C bath following a standard freeze. The temperature scale on the left-hand side of the figure is associated with the upper curve; the scale running from 28562000 to 28567000 on the right-hand side of the figure is associated with the middle curve; and the other scale on the right-hand side is associated with the lowest curve.

We attribute this melting behavior to the melting of the gallium mantle from the top of the cell downward. Upon complete melting of the gallium, the sample temperature approached the bath temperature exponentially. The melting behavior of each sample was reproducible and the details of the melting curves at the highest resolution were strongly characteristic of each sample. There are at least two important factors which influence the shape of these curves. One is the impurities and their distribution, as determined by the sample's prior thermal treatment, and the second is the establishment of the

hydrostatic head, which varies from cell to cell. The latter factor affects the initial portion of the melting curve and the first factor affects the melting range of the sample. Although most melting curves were very similar, both in shape and in melting range, to those reported earlier for the gallium samples in the all-plastic cells[1], some samples definitely had a larger melting range. We interpreted this as probably being due to impurities introduced into the sample through pin-holes in the Teflon covering the thermometer well since 6 of the 7 samples were from the same supplier and were presumably of the same purity. The lower triple-point temperatures observed for those same samples confirm the presence of more impurities in those samples. Although the results from the melting curves agree qualitatively with the results of the comparison of the triple-point temperatures, it is difficult to make a quantitative comparison of the samples based purely on the melting behavior.

Melts were obtained also for gallium mantles (of the less pure samples) which had been rapidly frozen. As expected, the curves were characterized by a flat plateau due to a uniform distribution of the impurities present, rather than by the non-flat "plateau" characteristic of impure samples.

A melting curve was obtained also for a gallium sample in a steel cell which had been prepared for measurement of the triple-point temperature. After preparation of the triple point, the cell was connected to the vacuum system and continuously pumped, an SPRT was placed in the thermometer well, the assembly placed in a 40 °C oil bath, and the gallium melted. As observed and reported previously[1] for gallium in the all-plastic cells, the temperature in the thermowell remained perfectly constant, to within our resolution of ±1.5 μ°C, until an abrupt rise several hours after the cell was placed in the 40 °C oil, which we attribute to penetration of the mantle by liquid gallium. This constancy of the triple-point temperature is important in that when the triple point of a sample, whether in an all-plastic cell or in a steel cell, is prepared as described earlier, the temperature of that triple point is independent of time and of the fraction of gallium melted.

Intercomparison of Gallium Samples

For a given set of gallium mantles, at least five comparison measurements using dc techniques were made for each sample, relative to the Alusuisse sample (F17/220) in the all-plastic cell, and two comparison measurements were made using ac techniques. Such comparisons were made on 6 different mantles of each sample, with the exception of the Eagle-Picher sample (J-57-76) for which only five different mantles were investigated by dc techniques. The results are given in Table III. A given number in the column headed dc under each sample is the mean value of the five dc comparison measurements for a given mantle; that number in the same row of the Table as just discussed and in the column headed ac under each sample is the mean value of the two ac comparison measurements for that same mantle. The other numbers in a given column refer to the mean values of the measurements for the different mantles of the sample.

It can be seen that the results obtained for the Alcoa (3809B) and the Eagle-Picher (J-57-76) samples (samples in all-plastic cells) are in good agreement with those obtained previously[1]. All of the samples in the steel cells have triple-point temperatures which are lower than those in the all-plastic cells. Since all of the Alcoa samples in the steel cells were supposedly of equal purity and the same as that of the Alcoa sample (3809B) in the all-plastic cell and since the Alusuisse samples were supposedly of the same purity, we conclude that the Teflon coating of the stainless steel thermowells must have had some pin-holes, which then allowed the gallium to become contaminated. Samples 3854 and 8002 appear to have considerably more impurities than the other samples.

Table III. Results of direct comparisons of triple-point temperatures for different mantles of each of the 10 gallium samples using both ac and dc techniques. Samples F17/220, 3809B and J-57-76 were in all-plastic cells; the remaining samples were in steel cells. The temperature differences are expressed in $\mu°C$.

ΔT(μ°C) F17/220-3809B		ΔT(μ°C) F17/220-(J-57-76)		ΔT(μ°C) F17/220-F17/252		ΔT(μ°C) F17/220-3854		ΔT(μ°C) F17/220-3855		ΔT(μ°C) F17/220-3856		ΔT(μ°C) F17/220-3860		ΔT(μ°C) F17/220-8002		ΔT(μ°C) F17/220-8005	
ac	dc	ac	dc	ac	dc	ac	dc	ac	dc	ac	dc	ac	dc	ac	dc	ac	dc
19	35	4		37	79	92	146	60	101	14	76	21	105	163	192	20	119
-35	-26	-14	9	-37	15	48	121	-26	17	23	79	5	65	150	217	14	88
30	14	26	36	54	116	106	141	44	86	27	92	62	107	247	293	84	134
10	17	70	109	23	67	137	190	52	88	62	101	64	136	110	184	40	89
-12	-18	9	-5	-24	42	89	132	46	90	20	58	50	87	168	224	32	79
33	31	22	58	7	82	118	180	58	88	48	108	92	130	230	291	49	96

Mean±S.D. (S_D)

22±36	9±25	44±56	41±45	10±35	67±35	98±30	152±27	39±32	78±31	32±19	86±18	49±32	105±27	178±51	234±48	40±25	101±21

The scatter among the data obtained by dc techniques for a given mantle of a given sample is comparable to the scatter among the data for the different mantles of the same sample. Only two measurements were made by ac techniques on each mantle, but they showed much better agreement than did the dc results. The scatter among the data for the different mantles of a given sample, however, was comparable to that observed among the dc results. This may indicate a slight variability of the triple-point temperature with mantle preparation. By looking at the ac and dc results for a given mantle of a sample, it is clear that the ac measurements were affected by the presence of the metal surrounding the thermometer in the steel cells, as expected.

Two conclusions can be drawn from the comparison study. The first is that the gallium samples in the steel cells are less pure than those in the all-plastic cells, as deduced by the fact that their triple-point temperatures are lower. This is thought to be due to contamination from the steel thermowells because of the presence of pin-holes in the Teflon covering of the thermometer wells. Some samples appear to be more impure than others. These results are in qualitative agreement with the melting behavior of the different samples.

The second conclusion is that the scatter among the dc results (probably the most reliable results since the thermometer readings are influenced by the presence of metal near the platinum sensing element when ac techniques are used) for different mantles of the same sample is about the same as the scatter of the measurements on a given mantle of a sample and is about ±50 μ°C. This indicates that if indeed different mantles, each prepared in the usual way (as described earlier), of a given sample give rise to different triple-point temperatures, the scatter in those values is no greater than the scatter in the measurements on a given mantle. Thus, one would conclude that the scatter observed in these experiments is just that due to the SPRT and the resolution of the bridge.

Gallium Triple-Point Results

The gallium triple-point temperature ascertained in this investigation was determined from measurements on the Alusuisse sample (F17/220) in the all-plastic cell using five SPRTs. The temperatures determined for each SPRT were calculated from the zero-power resistance ratios using the standard interpolating formula specified by the IPTS-68, the SPRT calibration constants (given in Table II) provided by the NBS Platinum Resistance Thermometer Calibration Laboratory, and the appropriate corrections described below. The calculated temperatures obtained by both ac and dc techniques for the Alusuisse sample in the all-plastic cell are given in Table IV. These data for SPRTs 090, 369, 374 and 375 are plotted in Fig. 3. As indicated earlier, a few measurements were also made of the triple-point temperature of gallium sample F17/252 in a steel cell. Those calculated temperatures are also shown in Table IV. Since the results of a calibration of an SPRT are expressed relative to the SPRT resistance at the ice-point of water, $R_{H_2O}(0)$, and since our reference is the triple point of water, $R_{H_2O}(t.p.)$, it was necessary in deriving the gallium triple-point temperature to calculate $R_{H_2O}(0)$ of an SPRT from the measured $R_{H_2O}(t.p.)$. The temperature experienced by an SPRT in the water triple-point cell was not 0.01 °C, however, because of hydrostatic head effects. Thus, the resistances of the SPRTs is the gallium and water triple-point cells were corrected for the depression of the true triple-point temperatures due to the hydrostatic pressures exerted by the columns of liquids. For the water triple-point cell, the depression is 7 μ°C per cm of water above the point of measurement[2]. Since the height of the water column in our triple point of water cell, cell B-11-803, was approximately 28 cm, the depression amounted to 196 μ°C. The variations in the amount of ice comprising
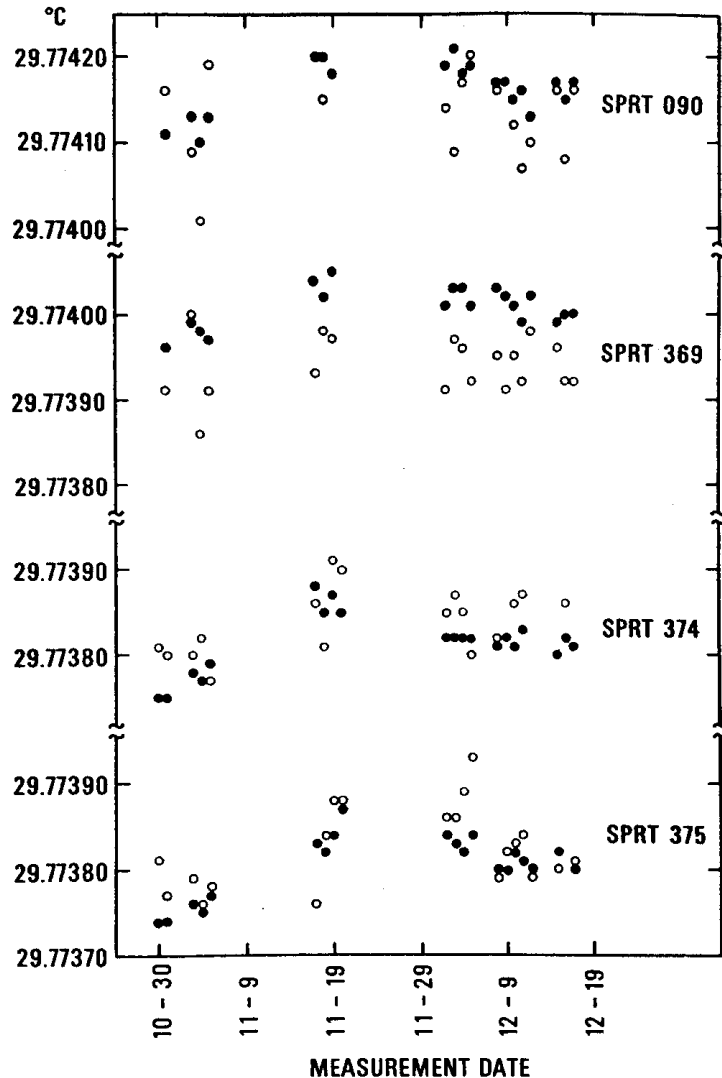

FIG. 3. Plots of the triple-point temperatures of gallium sample F17/220, obtained with SPRTs 090, 369, 374 and 375, as a function of the measurement date. Data plotted are from Table IV. ● represent the ac results, O represent the dc results, and θ represents ac and dc results that occur at the same point.

the mantle could cause an uncertainty of ±0.5 cm in the height of the water column, leading to an uncertainty of ±3.5 μ°C in the calculated hydrostatic pressure correction. The zero-power resistance of an SPRT determined in the triple-point of water cell and experiencing a temperature of 0.009804 °C was thus corrected to 0 °C by dividing that resistance by the appropriate resistance ratio, the W(t).

The depression of the temperature in the gallium triple-point cell due to the column of liquid gallium at the triple-point temperature was calculated from the results reported previously[1] and confirmed in this investigation as 12 μ°C per cm of liquid gallium. The height of the liquid gallium column in the all-plastic cell was approximately 13 cm and that height results in a depression of 156 μ°C. The height of the liquid gallium column in the steel cell was approximately 13.5 cm, resulting in a temperature depression of 162 μ°C. These values of depression, either 156 μ°C or 162 μ°C, were added to the temperatures actually measured in the respective gallium triple-point cell (and calculated as indicated above for the appropriate resistance ratio).

We have included in Table IV the temperatures determined by using ac techniques. Note the fairly good agreement of these values with those determined by dc

Table IV. Tabulation of triple-point temperatures (°C) determined for samples F17/220 (in an all-plastic cell) and F17/252 (in a steel cell) by using ac and dc techniques. See text for details of calculation.

SPRT:	089		090		369		374		375	
Date	ac	dc	ac	dc	ac	dc	ac	dc	ac	dc
Data for F17/220										
10/30/80							29.77375	29.77381	29.77374	29.77381
10/31/80			29.77411	29.77416	29.77396	29.77391	29.77375	29.77380	29.77376	29.77377
11/03/80			29.77413	29.77409	29.77399	29.77400	29.77378	29.77380	29.77379	29.77379
11/04/80			29.77410	29.77401	29.77400	29.77386	29.77377	29.77382	29.77375	29.77376
11/05/80			29.77398	29.77419	29.77398	29.77391	29.77379	29.77377	29.77377	29.77378
11/17/80			29.77413	29.77420	29.77397	29.77393	29.77388	29.77386	29.77383	29.77376
11/18/80			29.77420	29.77415	29.77404	29.77398	29.77385	29.77381	29.77382	29.77384
11/19/80			29.77420	29.77418	29.77402	29.77397	29.77387	29.77391	29.77384	29.77388
11/20/80			29.77418		29.77405		29.77385	29.77390	29.77387	29.77388
12/02/80			29.77419	29.77414	29.77401	29.77391	29.77382	29.77385	29.77384	29.77386
12/03/80			29.77421	29.77409	29.77403	29.77397	29.77382	29.77387	29.77383	29.77386
12/04/80			29.77418	29.77417	29.77403	29.77396	29.77382	29.77385	29.77382	29.77389
12/05/80			29.77419	29.77420	29.77401	29.77392	29.77382	29.77380	29.77384	29.77393
12/08/80			29.77417	29.77416	29.77403	29.77395	29.77381	29.77382	29.77380	29.77379
12/09/80			29.77417	29.77417	29.77402	29.77391	29.77382	29.77382	29.77380	29.77382
12/10/80			29.77415	29.77412	29.77401	29.77395	29.77381	29.77386	29.77382	29.77383
12/11/80			29.77416	29.77407	29.77402	29.77392	29.77383	29.77387	29.77383	29.77384
12/12/80			29.77413	29.77410	29.77399	29.77398			29.77384	29.77379
12/15/80			29.77417	29.77416	29.77402	29.77396	29.77380	29.77380	29.77380	29.77380
12/16/80			29.77415	29.77408	29.77399	29.77392	29.77382	29.77386	29.77382	
12/17/80			29.77417	29.77416	29.77400	29.77392	29.77381	29.77381	29.77380	29.77381
12/18/80	29.77422	29.77412								
12/18/80	29.77421	29.77424								
12/18/80	29.77421	29.77417								
12/18/80	29.77422	29.77422								
12/19/80	29.77420	29.77415								
12/19/80	29.77411	29.77408								
12/19/80	29.77421	29.77418								
Data for F17/252										
01/14/81					29.77399	29.77386	29.77381	29.77388	29.77377	29.77375
01/16/81					29.77397	29.77388	29.77377	29.77376	29.77376	29.77372

Table V. Average triple-point temperature (°C), standard deviation (S_D) and standard deviation of the mean ($S_{\bar{D}} = S_D/\sqrt{n}$ where n = number of data points) for each SPRT in the Alusuisse gallium sample (F17/220) in the all-plastic cell determined by ac and dc techniques.

SPRT	ac			dc		
	Temp. (°C)	S_D	$S_{\bar{D}}$	Temp. (°C)	S_D	$S_{\bar{D}}$
089	29.774197	±0.000039	±0.000015	29.774166	±0.000055	±0.000021
090	29.774163	±0.000031	±0.000007	29.774137	±0.000051	±0.000012
369	29.774008	±0.000024	±0.000005	29.773938	±0.000040	±0.000009
374	29.773814	±0.000035	±0.000008	29.773835	±0.000037	±0.000008
375	29.773805	±0.000036	±0.000008	29.773825	±0.000047	±0.000011
Avg.	29.773997	±0.000162	±0.000018	29.773980	±0.000143	±0.000016

techniques. Although ac measurements of temperature are generally less reliable than dc measurements, we believe the agreement confirms that the SPRTs were dry. Their ac behavior at the triple point of water lends further evidence to this interpretation.

We have listed in Table V the average temperature, its standard deviation (S_D) and the standard deviation of the mean ($S_{\bar{D}}$) derived from ac and dc measurements for each of the 5 SPRTs in the Alusuisse sample (F17/220) in the all-plastic cell. The total spread of 0.34 m°C among the dc values from the 5 SPRTs would at first glance seem rather surprising. Differences may be expected among the thermometers, however, and they may arise from three sources. For measurements of a given SPRT, the uncertainty arising from calibration errors (calibrated against fixed points of the IPTS-68 as maintained at NBS) may be as large as ±0.21 m°C. Another source of error is the possible presence of moisture on the thermometer insulation. The error from this effect would vary from thermometer to thermometer. Although we think the error from this source is small in our case, it has been demonstrated[21] that it can cause an error at the triple point of water equivalent to +0.0 or -0.5 m°C without the thermometer having a detectable "wet kick." Then, of course, different SPRTs may indicate discrepant temperatures at fixed points intermediate to the calibration points due to the use of real, non-ideal, materials. Here again, we would expect the error from this source to be small compared to 0.1 m°C near 30 °C. Considering these sources of error, then, we might expect our SPRTs to indicate temperatures of a given intermediate fixed point near 30 °C that differ by approximately 0.4 m°C to 0.5 m°C. Thus, the differences in the temperatures indicated by the different SPRTs are not inconsistent with these error estimates.

As indicated previously[1], it is thought that the Alusuisse sample (F17/220) in the all-plastic cell is the purest sample that we have and the effects of impurities in that sample would be to depress the melting temperature by less than 0.01 m°C. The triple-point temperature of that sample, then, most closely represents the triple-point temperature of pure gallium. That value determined in this investigation through the use of 5 SPRTs is 29.77398 °C with a standard deviation of all data points of ±0.00014 °C and a standard deviation of the mean of ±0.00002 °C. The standard deviation of the data for individual SPRTs range from ±0.000037 to ±0.000055 °C.

The measured triple-point temperature of sample F17/252 in a steel cell is given in Table VI and is consistent with the direct comparison results. Table VII compares the dc results of the two Alusuisse samples.

A comparison of the gallium triple-point temperatures obtained with the same SPRTs used in this investigation and in that reported previously[1] is given in Table VIII. Note that the temperatures obtained in this investigation are lower than those reported earlier. We attribute this to the presence of moisture in the SPRTs when the previous results were obtained. The magnitude of the change is not inconsistent with this assumption.

Discussion of Errors

The triple-point temperature of gallium measured on the IPTS-68 in this investigation is subject to uncertainties from several potential sources of systematic errors. They arise from SPRT calibrations, bridge inaccuracy, impurities, moisture on the SPRT insulation, and variations in isotopic composition.

The uncertainties in realizing the fixed points of the IPTS-68 which were used in the calibration of the SPRTs are ±0.1 m°C for the triple point of water[2,19] and ±1 m°C for the freezing points of tin and zinc[19]. The combination of these results gives an uncertainty from calibration of ±0.4 m°C. The estimated inaccuracy of the dc bridge, discussed earlier, corresponds to an uncertainty in the temperature measurements of ±0.16 m°C. In consideration of the arguments given earlier, the uncertainty resulting from impurities in the Alusuisse sample in the all-plastic cell is estimated to be less than ±0.01 m°C[1]. Although there is the possibility of the presence of moisture on the SPRT insulation[21], we believe that in view of our treatment of the SPRTs prior to the triple-point temperature measurements, the uncertainty from this source is negligible. Variations in isotopic composition of the gallium samples would affect the triple-point temperature, but since there is no information available regarding the magnitude of such an effect, it is not possible to make a realistic estimate of the uncertainty arising from this source. We would expect this uncertainty to be small, however, since the isotopic ratios $^{69}Ga/^{71}Ga$ of the Alcoa and the Alusuisse samples used to fill the cells were generally in very close agreement[22] and the differences bore no correlation with the measured triple-point temperatures. The source of the uncertainty in the triple-point temperature of water, mentioned above under discussion of errors in calibration, is the variation of the triple-point temperature with isotopic composition. Although

Table VI. Average triple-point temperature (°C), standard deviation (S_D) and standard deviation of the mean ($S_{\overline{D}} = S_D/\sqrt{n}$ where n = number of data points) for 3 SPRTs in the Alusuisse gallium sample (F17/252) in the steel cell determined by ac and dc techniques.

SPRT	ac			dc		
	Temp. (°C)	S_D	$S_{\overline{D}}$	Temp. (°C)	S_D	$S_{\overline{D}}$
369	29.773980			29.773870		
374	29.773790			29.773820		
375	29.773765			29.773735		
Avg.	29.773845	±0.000106	±0.000043	29.773808	±0.000073	±0.000030

Table VII. Comparison of triple-point temperatures for Alusuisse gallium samples in the all-plastic cell (sample F17/220) and in the steel cell (sample F17/252) (dc results).

SPRT	All-plastic cell (°C)	Steel cell (°C)	ΔT (m°C)
369	29.773938	29.773870	0.068
374	29.773835	29.773820	0.015
375	29.773825	29.773735	0.090
Avg.	29.773866	29.773808	0.058

Table VIII. Comparison of present dc results on triple-point temperature with those reported previously for the Alusuisse sample in the all-plastic cell (sample F17/220).

SPRT	Values from present study (°C)	Previously reported values (°C)	ΔT (m°C)
089	29.77417	29.77421	0.04
374	29.77384	29.77395	0.11
375	29.77383	29.77402	0.19
Avg. (from listed SPRTs above)	29.77395	29.77406	0.11
Avg., S_D (5 SPRTs for present results and 3 SPRTs for previous study)	29.77398±0.00014	29.77406±0.00011	0.08

this uncertainty would normally be included again in temperature measurements with SPRTs, it is inappropriate to include this uncertainty a second time here since the water triple-point cell used in these measurements came from the same source as those used in the SPRT calibrations. The total uncertainty from all of these sources for which we can make estimates is ±0.6 m°C.

The systematic and random uncertainties comprise the total uncertainty and is about ±0.7 m°C for our measurements.

SUMMARY AND CONCLUSIONS

An intercomparison of 10 gallium cells using one SPRT, and a new determination of the triple-point temperature of high-purity gallium using five newly-dried and then calibrated SPRTs were made. The 10 cells consisted of three all-plastic cells studied previously[1] (one containing Alusuisse sample F17/220, one Alcoa sample 3809B, and one Eagle-Picher sample J-57-76) and seven steel cells (one containing an Alusuisse sample and six containing Alcoa samples). The Alusuisse sample (F17/220) in the all-plastic cell has the highest-purity and its triple-point temperature was determined to be 29.77398 °C. From the results of the intercomparison of the triple-point temperatures of the samples and of the melting curves, we confirmed our previous assessment of the relative purity of the three samples in the all-plastic cells and determined that the samples placed in the steel cells were already or became contaminated. We believe they became contaminated by contact with the stainless steel thermowells by way of pin-holes in the Teflon coating. Consequently, we conclude that all-plastic cells or cells with non-metallic thermowells should be used in preparing triple-point cells for gallium. All triple-point temperature data obtained with the five SPRTs on the highest-purity sample, the Alusuisse sample (F17/220) in the all-plastic cell, have a standard deviation of ±0.00014 °C (and a standard deviation of the mean of ±0.00002 °C), although the standard deviations of the data for individual SPRTs range from ±0.000037 °C to ±0.000055 °C (and standard deviations of the means of data for individual SPRTs range from only ±0.000008 °C to ±0.000021 °C). We estimate the systematic uncertainty to be ±0.6 m°C. The differences in triple-point temperatures indicated by the different SPRTs are due to calibration errors and/or to different behavior of the platinum sensing elements at points intermediate to the calibration fixed points of the IPTS-68. From these results, we conclude that more fixed points (perhaps Ga, In and Cd triple points) should be defined for the next IPTS for the use of those who desire high precision and accuracy.

The hydrostatic pressure effects were measured and were in agreement with the previously reported[1] pressure dependence of the melting point.

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REFERENCES

*   Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

1. Mangum, B.W. and Thornton, D.D., Metrologia 15, 201 (1979).

2a. Comptes rendus des séances de la Treizième Conférence Générale des Poids et Mesures, Annexe 2, p. Al (1967-1968).

2b. Comité Consultatif de Thermométrie, 8e Session, 1967, Annexe 18.

2c. Metrologia 5, 35 (1969).

2d. Comptes rendus des séances de la Quinzième Conférence Générale des Poids et Mesures, Résolution 7, p. 105, Annexe 2, p. Al (1975).

2e. Metrologia 12, 7 (1976).

3. Lecoq de Boisbaudran, P.E.: Comp. Rend. 81, 493 (1875).

4. Lecoq de Boisbaudran, P.E.: Comp. Rend. 82, 1036 (1876); Comp. Rend. 83, 611 (1876).

5. Richards, T.W., Boyer, S.: J. Am. Chem. Soc. 43, 274 (1921).

6. Craig, W.M., Drake, G.W.: J. Am. Chem. Soc. 56, 584 (1934).

7. Roeser, Wm. F., Hoffman, J.I.: J. Res. NBS 13, 673 (1934).

8. Hoffman, J.I.: J. Res. NBS 13, 665 (1934).

9. Jach, J., Sebba, F.: Trans. Faraday Soc. 50, 226 (1954).

10. Boedtker, O.A., La Force, R.C., Kendall, W.B., Ravitz, S.F.: Trans. Faraday Soc. 61, 665 (1965).

11. Pennington, P.R., Ravitz, S.F., Abbaschian, G.J.: Acta Met. 18, 943 (1970).

12. Pashaev, B.P.: Fiz. Tverd Tela 3, 416 (1961).

13. Wenzl, H., Mair, G.: Z. Phys. B21, 95 (1975).

14. Abbaschian, G.J., Ravitz, S.F.: J. Cryst. Growth 28, 16 (1975).

15. Thornton, D.D., Mangum, B.W.: Procès Verbaux du CCT, Document No. CCT/76-13, June, 1976.

16. Lau, S., Schlott, P.: Procès Verbaux du CCT, Document No. CCT/76-23 June, 1976.

17. Sostman, H.E.: Rev. Sci. Instrum. 48, 127 (1977).

18. Thornton, D.D.: Clin, Chem. 23, 719 (1977).

19. Riddle, J.L., Furukawa, G.T., Plumb, H.H.: Platinum resistance thermometry, NBS Monograph 126, 1973, Supt. of Documents, U.S. Government Printing Office, Washington, D.C. 20402.

20. Cutkosky, R.D.: J. Res. NBS 74C, 15 (1970).

21. Berry, R.J.: Metrologia 2, 80 (1966).

22. Gramlich, J.W., Machlan, L.A., Private communication.